PROGRESS IN ENGINEERING CULTURED QUARTZ FOR USE BY THE CRYSTAL INDUSTRY

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SUMMARY

Beginning in 1945, with knowledge brought to this country from Germany of Professor Nacken's wartime adaptation of Professor Spezia's hydrothermal process for depositing quartz on a seed crystal, a continuous series of U. S. Signal Corps contracts has now established that cultured quartz in most cases is competitive technically and commercially with natural quartz. This commercial result is shown to be due to economies proceeding from the twin-free nature of cultured quartz and its uniformity of size and orientation which may be specified in advance by the purchaser on a commitment basis.

The history of commercial sales of cultured quartz is reviewed, leading to the present minimum price of $27.50 per pound established in June of 1958 for crystals suitable for use by the Crystal Industry. Manufacturers' material costs for even AT cuts derived from cultured quartz approach material costs derived from natural quartz. But net economies due to reduced labor and sawing charges are definitely attractive, and amount to 20-25% in even AT rough cuts. In the cases of +5° X-cuts, NT cuts and JT cuts, these net economies are enhanced.

In addition, the same production runs by manufacturers have shown attractive uniformity in electrical properties of the finished oscillators. The controlled hydrothermal process of industry compared to the widely varying process of nature is believed to promise the Crystal Industry additional applications for oscillators and filters not now possible.

The present I.P.M. contract is making satisfactory progress toward the use of domestic high-purity polycrystalline feed material for producing cultured quartz. Another objective of the current I.P.M. contract is the production of quartz crystals consisting solely of growth in the direction of the Z-axis.

Viewed in perspective, the accomplishments to date reinforce the promise of equally important progress in the future.

INTRODUCTION

My interest in our current project of producing and selling artificially grown quartz really began in 1945 when I was visiting Germany. This visit was under the auspices of the

U. S. Army, expressed through its Technical Industrial Intelligence Committee, primarily to determine what the Germans were doing with beryllium. As I was equally interested in commercializing piezoelectric Rochelle salt and other crystals deposited from aqueous solutions, I was pleased to hear of Professor Nacken's continuation of Professor Spezia's work with hydrothermally deposited quartz, and visited him at Schramberg. My subsequent report stimulated the late Colonel Swinnerton, of Antioch, to visit Germany confirming and extending the information. His favorable impressions resulted in the inauguration of the series of contracts for growing quartz which have been sponsored by the U. S. Army Signal Corps and reported every year at these Symposia. In 1945, there was scant hope of developing a process whose product would have sufficient merit to compete with natural quartz except in a wartime economy. The attainment of the results which I am about to present are a tribute to the farsighted tenacity of the U. S. Army Signal Corps.

CULTURED AND NATURAL QUARTZ GENERALLY CONTRASTED

Quartz which was deposited in nature, although essentially in a hydrothermal process, was not controlled during its deposition as to the many pertinent variables. The resulting product must also be variable, not only in size and shape but also in quality. This probably accounts for the very limited number of natural occurrences of electronic grade quartz.

But synthetic or cultured quartz, on the other hand, as industrially deposited in a hydrothermal process, may be closely controlled. From this it immediately follows that cultured quartz will be as uniform as are the controls applied during deposition. It has been established that if the seed is twin-free, so also, for practical purposes, is the resulting crystal. Moreover, if the seed is of a given cut and size, and if the conditions of deposition are fixed, the resulting quartz crystals will be uniform in size, shape and quality. Full information is not yet in hand correlating all the properties of cultured quartz with the controlling variables, but progress in this respect is being maintained. For instance, under any given set of conditions, the production of "blue haze," or the Tyndall effect, is associated with higher growth rates, and the quartz deposited on the seed in the minus-direction of the X-axis is the most susceptible to its generation.

At present our organization is offering a number of sizes of twin-free quartz crystals whose central, long dimension is parallel to the Y-axis or departs therefrom by a specified amount. The specifications as to size and orientation of the Y-axis are approximately fixed by the kind of cut and dimensions which it is intended to produce. Successful applications of cultured quartz are now being made commercially to the following cuts: AT, +5° X, NT, and JT.

The price of cultured quartz crystal bar varies somewhat with the specifications, but is generally higher per pound than for natural quartz of electronic grade. It is therefore necessary to experience convincing total economies in combined cost of labor and materials, if the cultured product is to find commercial acceptance.

AT CUTS FROM CULTURED QUARTZ

The case for AT cuts will be presented for illustration, as economical margins are here less easy to attain than in the cases of the more specialized cuts normally using larger and higher-priced crystals of natural quartz. The AT blanks to which the data given below apply are rough cut to .430" diameter. The cultured quartz crystal bar employed had the following dimensions:

.75" in the direction of the Z-axis
.50" " " " " " X-axis
5.5" " " " " " Y-axis

The two long boundary edges of the surface grown in the minus-direction of the X-axis lay within 1° of the direction of the Y-axis, and these edges were used as reference lines for rough orientation.

Figure 1 shows line drawings of the crystal bar under discussion, with the axes indicated. Also shown is the direction of the AT cut. Cross-sectional views (d) and (e) show the position of the seed. A preparatory operation of "mud-wheeling," or grinding, has removed the crown of the surface grown in the minus X-direction, as shown in line drawing (e).

Figure 2 shows the crystal with this "mud-wheeled" surface cemented directly to a wooden holding-block mounted on a transfer fixture. Figure 3 shows this assembly on the orienting table of an X-ray goniometer. A "continuous bonded" 30 mil thick 6" diameter diamond saw was used in obtaining the results which follow, but gang sawing is desirable, as in Figure 4 showing a modified Brown & Sharpe surface grinder.

Figure 5 shows the actual wafers produced from this crystal bar which weighed 82 grams, or 0.18 pounds. Outline circles (.430" diam.) of the corresponding blanks, 118 in number, appear on the wafers. This yield is at the rate of 653 AT blanks per pound of cultured quartz.

Figure 6 graphically expresses the yields per pound of cultured quartz which it is possible to obtain at various diameters of rough AT blanks. The solid line and solid circles represent the actual experience of industry. The dashed line and open circles represent the original determination as run at Sawyer Research Products -- also attained industrially in the case of the .400" rough-cut square blank. Note that in small diameters (.310"), yields can reach 900 per pound.

Figure 7 shows a projection view of AT circles of two different finished diameters on a plane perpendicular to the direction of the Y-axis. This leads to the tabulation of the most economical widths of cultured crystal bar which should be employed for various diameters of AT crystal oscillators.

In the case of 35 mil thick AT rough cut blanks measuring .400" on a side, the yield was 670 blanks per pound of cultured quartz using 30 mil saws.

Important savings in labor in producing rough cut blanks flow from the use of cultured quartz bars due to the following principal factors:

1. Uniformity of size, shape, handedness, and orientation (within 1°).

2. Freedom from twinning, both optical and electrical.

3. Specified size of bar adjusted to blank size for minimum sawing and wastage.

4. Elimination of deep saw cuts, resulting in less saw wear, smoother cut surfaces and less lapping.

5. Facilitated X-ray orientation.

6. Reduced rejections due to increased uniformity in electrical properties of oscillators produced.

There is also the associated advantage of a reduction in the amount of capital equipment required due to increased efficiency of its use.

Cost

By the kind permission of The James Knights Company, we may report the following figures obtained by them in a production run utilizing cultured quartz:

Raw Material: Cultured quartz bars at $27.50 per lb.

Product: Rough cut AT blank

Size: 0.400" square (rough cut dice) x .035" thickness

Saw: 0.030" continuous bonded

Yield: 670 blanks per lb. -- 797% greater than for natural quartz (84 blanks per pound)

Cost of Material: 17% greater than for natural quartz
Cost of Labor: 41% less than for natural quartz
Over-all cost: 23% less than for natural quartz

These figures take no account of savings effected due to increased saw life, fewer mounting plates, etc.

So far as is known to the author, all commercial sales of cultured quartz, at least in this country, have been made by organizations functioning under his direction. The price of $27.50 per pound referred to in the preceding table was established by Sawyer Research Products in June of 1958. The first sale at this price was on July 14, 1958. The first sale of cultured quartz of which we have a record was on May 3, 1955, at $52.50 per pound, through The Brush Laboratories Company, then a unit of Clevite Corporation. Numerous other intermediate sales took place. These prices refer to crystal bar of a size suitable for use by the Crystal Industry for its oscillators. Larger sizes and other special conditions operate to increase these minimum prices.

OTHER CUTS

Reverting now to the subject of cuts other than AT, our organization believes that the larger or more specialized the cut, the greater are the economies which can be realized. A case in point is the so-called +5° X-cut. Crystal bar grown explicitly for this purpose is deposited on seeds cut with their long edges at +5° to the Y-axis, as shown in Figure 8. It is apparent that maximum convenience and maximum utilization of the cultured quartz bar is thus obtained.

Crystal bar for +5° X-cuts may be supplied with right- or left-handedness, as specified, and is thus very well-suited for the manufacture of JT crystal assemblies.

OUTLOOK

Reported in these Symposia on numerous occasions has been the variable behaviour of both natural and cultured quartz crystal bars to X-ray irradiation, etching, and visual inspection for bubbles, etc. The observed variations exist not only from sample to sample but also within any one sample. In cultured quartz, as you will recall, X-ray irradiation and etching can distinguish and delineate the growth regions in the directions of the Z-axis and of the X-axis, both plus and minus. Chemical analysis locates maximum impurity content of some elements in the area of minus X-growth and minimum impurity in the areas of Z-growth. These variations appear to be greater from piece to piece of natural quartz than in cultured, which latter therefore shows greater uniformity of electrical properties. An objective of the present I.P.M. contract is to produce pure Z-growth. It is too early to report on progress in this objective beyond the statement that it is moderately satisfactory.

Another objective of the same I.P.M. contract is the production of high-grade cultured quartz from a domestic supply material instead of Brazilian Lascas. Results to date look promising, and we do not anticipate much difficulty in filling the terms of the contract with respect to the use of domestic supply material.

Figure 9 shows a crystal bar of cultured quartz 8" long in the direction of the Y-axis. Longer crystal bars are in the making and will, in due course, be offered commercially.

We feel confident that desirable basic electrical properties of cultured quartz will be attained which cannot be found in natural quartz, and that these superqualities will open the way to new applications of oscillators.

CONCLUSION

Cultured quartz now competes favorably with natural quartz in almost all cases, and time will benefit its relative position.

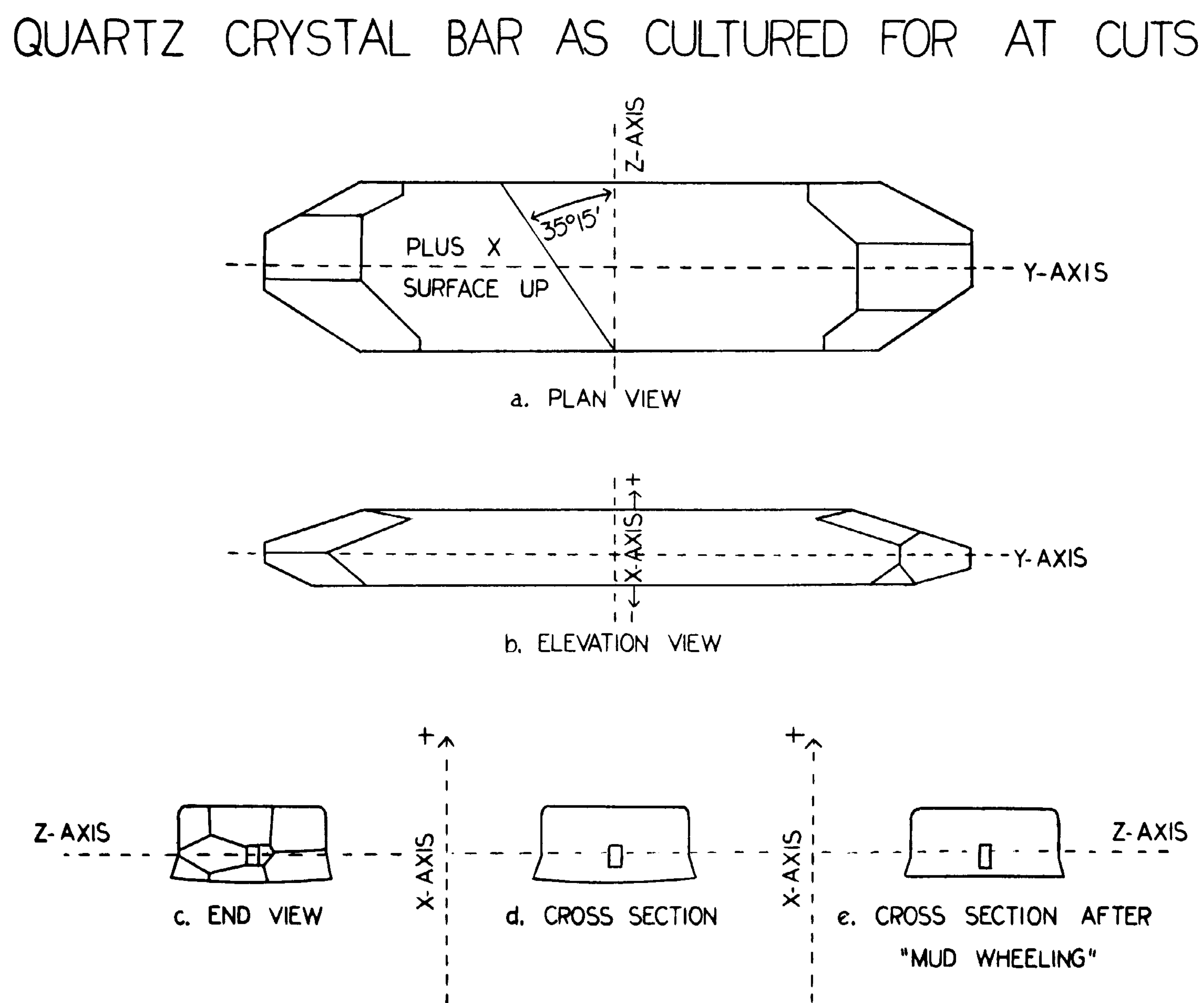


Fig. 1 Cultured quartz bar for AT rough cuts

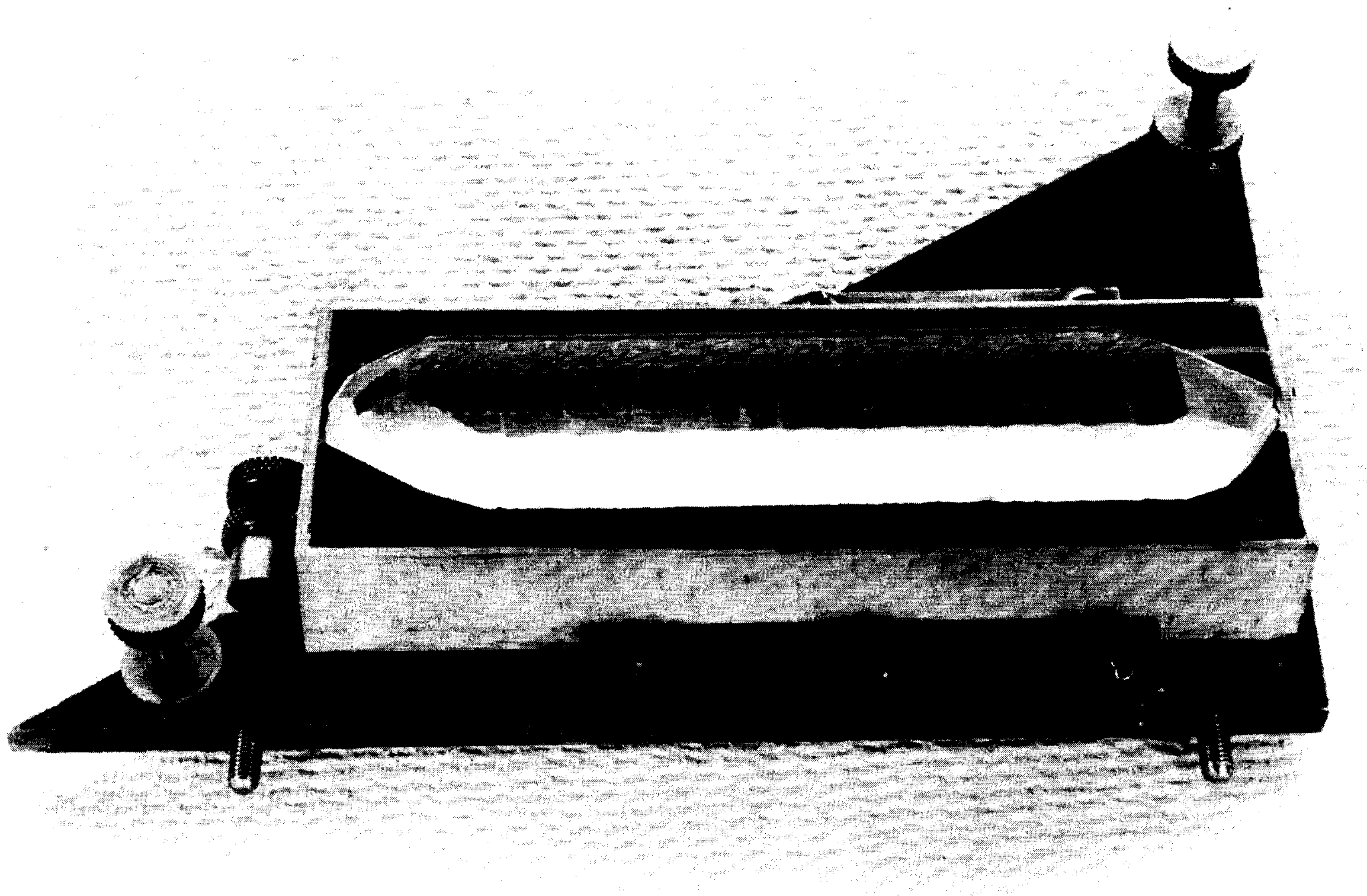


Fig. 2 Assembly of crystal bar, wood block and transfer jig

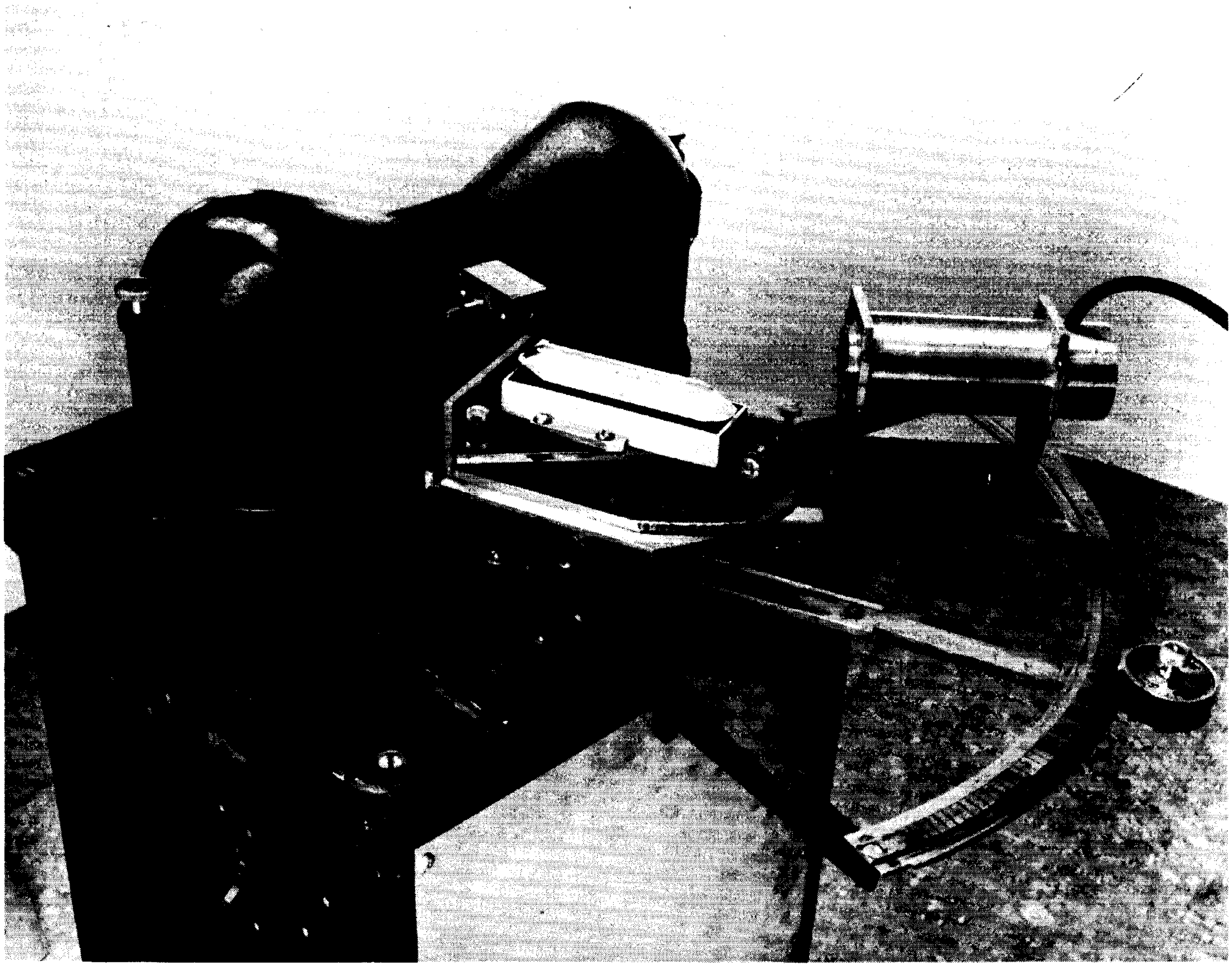


Fig. 3 Crystal bar and transfer jig on X-ray goniometer

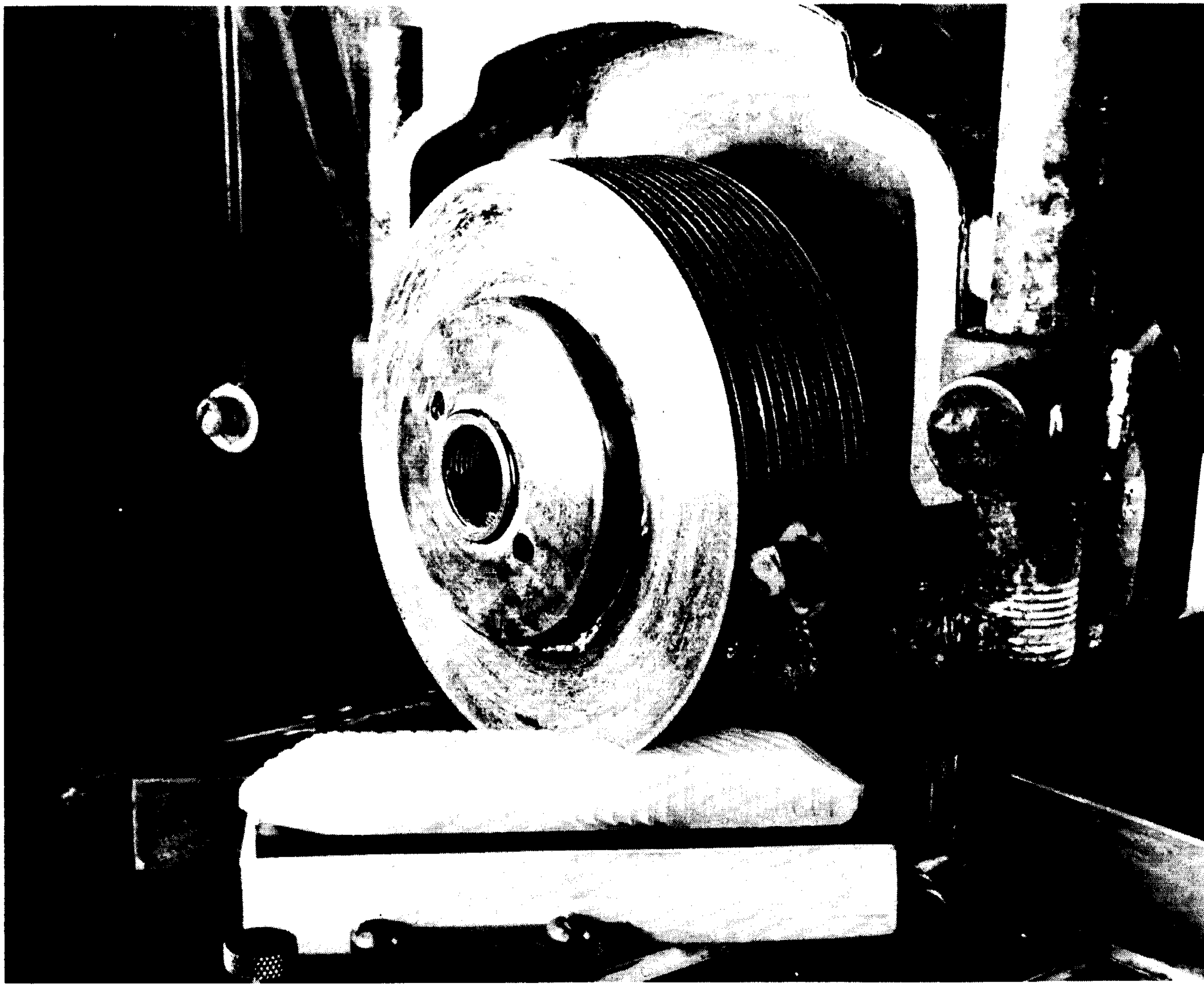
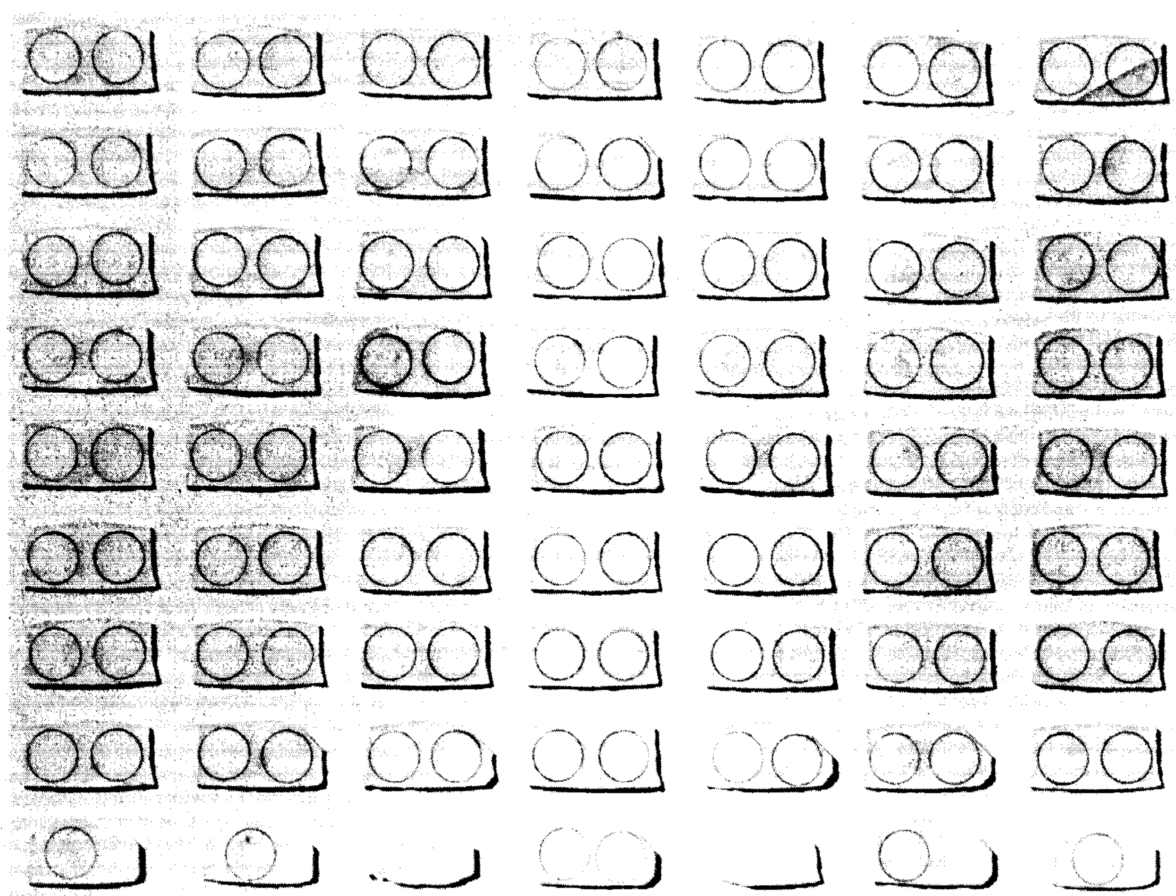


Fig. 4 Gang sawing of crystal bar for AT cuts



CRYSTAL BAR SIZE Y $5\frac{1}{2}$" Z $\frac{3}{4}$" X $\frac{1}{2}$"
CRYSTAL BAR WT. 82 Gm. SAW CUT .030"
AT BLANK THICKNESS .040"

118 - .430" DIA. AT BLANKS PER CRYSTAL BAR
653 - .430" DIA AT BLANKS PER POUND

Fig. 5 Wafers from 82 g. cultured quartz bar -- 118 blanks .430" diam. Yield per pound, 653 blanks

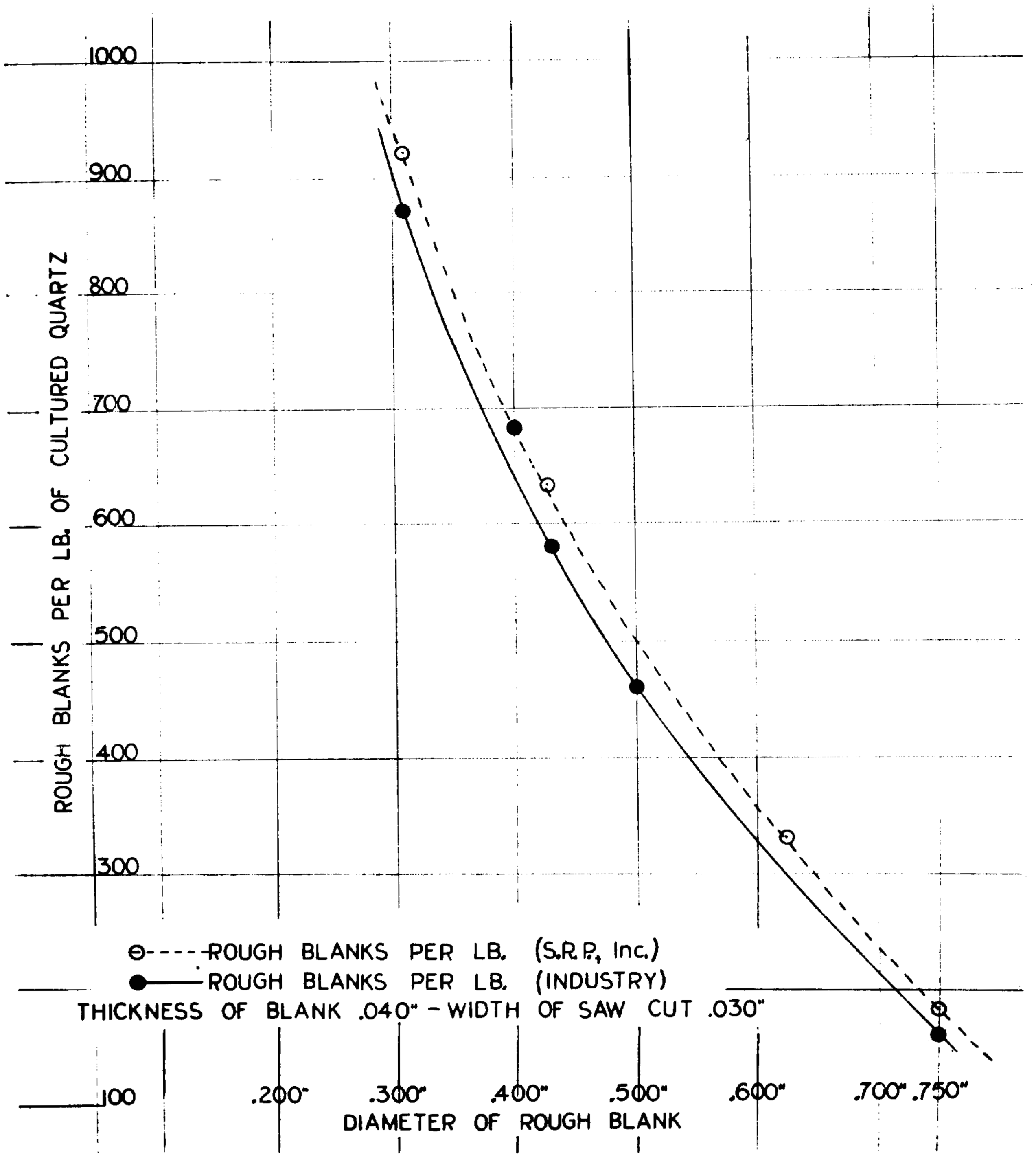
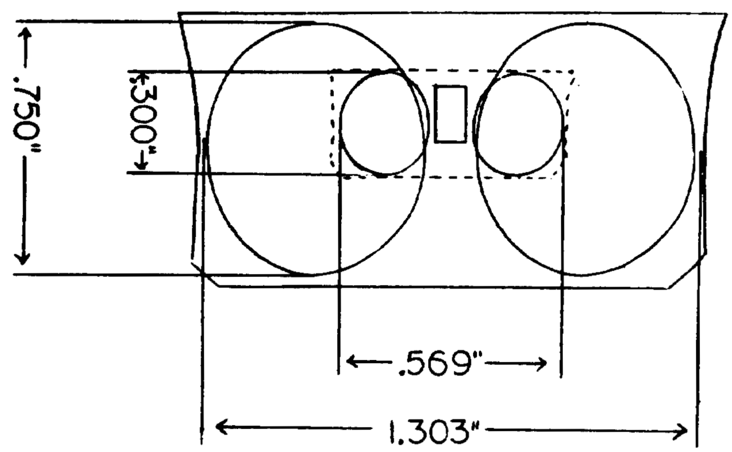


Fig. 6 Yield of AT cut blanks per pound of cultured quartz related to blank diameters

PROJECTION OF AT ROUGH CUT BLANKS OF .750" DIAMETER AND .300" DIAMETER ON PLANE SECTION OF CORRESPONDING CRYSTAL BAR LYING PERPENDICULAR TO Y-AXIS



ROUGH CUT AT BLANK DIA.	MIN. WIDTH OF CRYSTAL BAR IN THE DIRECTION OF THE Z-AXIS
.300"	.569"
.320"	.602"
.430"	.775"
.500"	.896"
.600"	1.058"
.650"	1.140"
.700"	1.222"
.750"	1.303"

Fig. 7 Projection of AT sections on plane perpendicular to Y-axis, with tabulation

CULTURED QUARTZ CRYSTAL BARS FOR +5° X CUTS AND JT CUTS

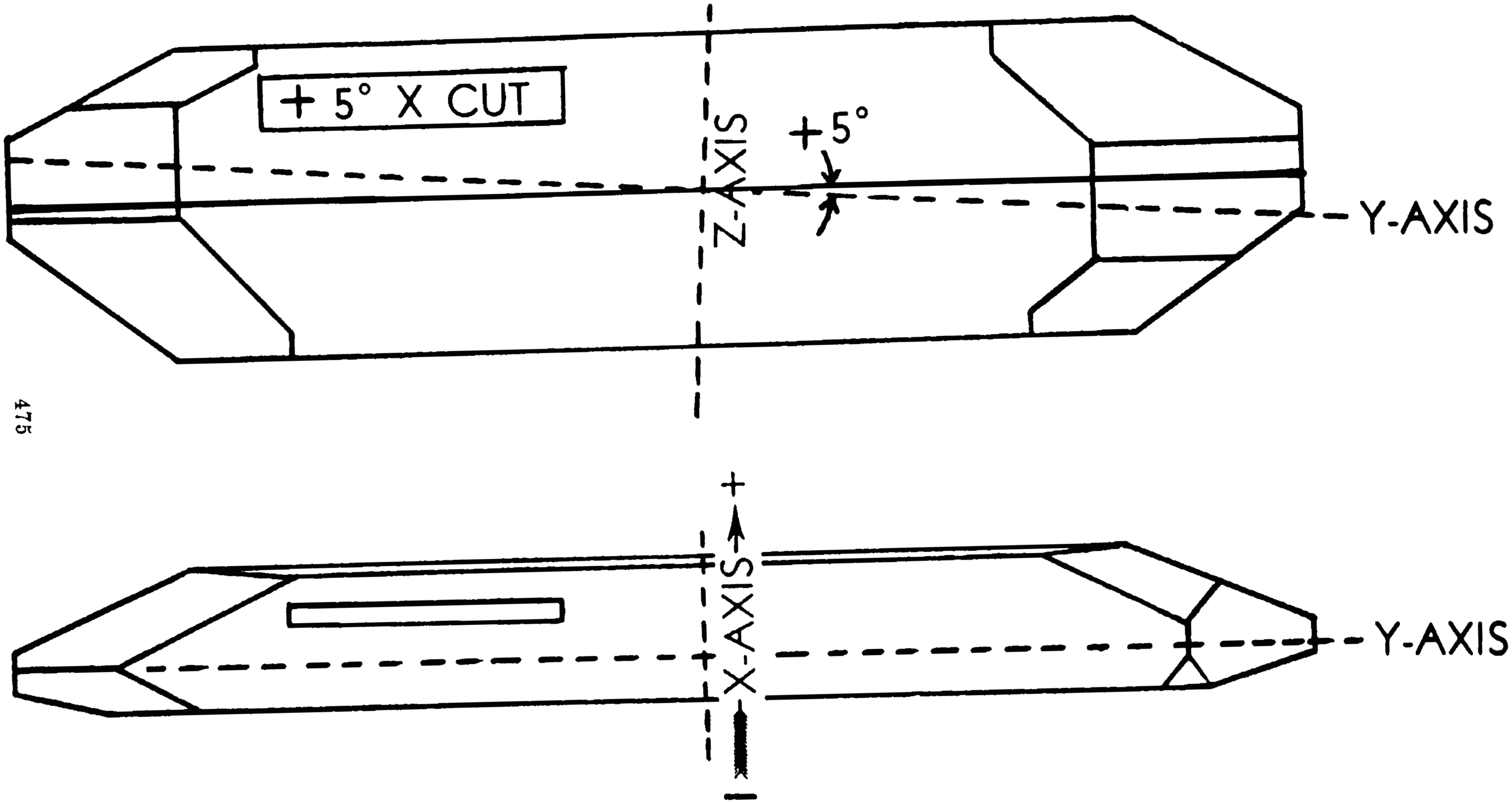


Fig. 8 Cultured quartz bar custom-grown for +5° X-cuts

Fig. 9 Cultured quartz bar 8" long in direction of Y-axis